IV.F.4 Plate-Based Fuel Processing System

David Yee (Primary Contact), Ralph Dalla Betta, Carlos Faz, Tek Ho, Helen Liu, Yafeng Liu, Jacques Nicole, Chris Pickett
Catalytica Energy Systems
430 Ferguson Drive
Mountain View, CA 94043
Phone: (650) 940-6321; Fax: (650) 965-4345; E-mail: DYee@CatalyticaEnergy.com

DOE Technology Development Manager: Donna Ho
Phone: (202) 586-8000; Fax: (202) 586-9811; E-mail: Donna.Ho@ee.doe.gov

Technical Advisor: Walt Podolski
Phone: (630) 252-7558; Fax: (630) 972-4430; E-mail: Podolski@cmt.anl.gov

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National Fuel Cell Research Center, Irvine, CA

Objectives

- Develop reactor designs and catalyst systems for the direct steam reforming of gasoline to a hydrogen-containing stream for a proton exchange membrane fuel cell.
- Develop computer simulation models of these systems to predict and optimize performance.
- Develop and test prototype reactors in a 1- to 10-kW(e) size range and demonstrate DOE target performance with emphasis on fast startup and rapid transient response.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I.   Fuel Processor Startup/Transient Operation
- J.   Durability
- L.   Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency
- N.   Cost

Approach

- Develop conceptual plate reactor designs for steam reforming, water gas shift and preferential CO oxidation.
- Develop catalyst washcoat compositions with the required activity, selectivity and durability consistent with the catalyst performance requirements specified by the simulations. Determine reaction kinetics for these catalyst compositions as required.
- Design and fabricate prototype plate reactors in the 1- to 10-kW(e) size range.
- Demonstrate plate reactor performance including startup, transient operation, efficiency and other performance factors.

Accomplishments

- Designed, fabricated, and tested a steam reforming plate reactor based on pre-existing heat exchanger plates. Completed installment of laboratory set-up to control flows, temperatures, and pressures of the prototype testing system.

- Generated 1.2 mol/min H_2 for 3-kW(e) prototype. Demonstrated 70-second startup time, reached DOE's 2004 target for turndown ratio (20:1) while maintaining a relatively constant internal reactor temperature, and performed a 20% load change within 1 second.

- Calculated integrated system efficiency of 79.5% and identified performance improvement targets to increase efficiency to as high as 83.6%.

- Determined the kinetic parameters of the steam reforming and combustion reactions.

- Demonstrated a reduction of CO to 10 ppm with an inlet CO concentration of 1.8% CO in a single-stage preferential CO oxidation reactor.

Future Directions

- Improve overall system control of the prototype steam reforming plate reactor to achieve a wider operating range and more precise degree of control. Develop and implement a model-based microprocessor control system to automate system control.

- Conduct additional tests with the 3-kW(e) steam reforming prototype reactor to decrease startup time, increase turndown ratio, and increase the step change transient capability.

- Design, fabricate, and test fin-folded 3-kW(e) steam reforming, water gas shift and preferential oxidation plate reactor prototypes, which will incorporate improvements learned from prior prototype(s).

- Reduce steam reforming catalyst cost while improving activity, durability, and operating range.

- Improve water gas shift catalyst activity and durability.

- Reduce preferential oxidation catalyst cost while improving activity and operating temperature range.

Introduction

On-board reforming of liquid fuels into hydrogen is an enabling technology that could accelerate consumer usage of fuel cell powered vehicles. The technology would leverage the convenience of the existing gasoline fueling infrastructure while taking advantage of the fuel cell's efficiency and low emissions. Commercial acceptance of on-board reforming faces several obstacles, including 1) startup time, 2) transient response, and 3) system complexity (size, weight and cost). These obstacles are being addressed in a variety of projects through development, integration and optimization of existing fuel processing system designs. Catalytica Energy Systems, Inc.'s (CESI's) project is directed at investigating steam reforming (SR), water gas shift (WGS) and preferential oxidation (PrOx) catalysts while developing plate reactor designs and hardware where the catalytic function is integrated into a primary surface heat exchanger.

SR, WGS and PrOx catalysts are being developed, studied and evaluated. A steam reforming prototype plate reactor was fabricated and assembled. The reforming catalyst driving the endothermic reaction is coated on one side of the thin plate while an oxidation catalyst is coated onto the other side of the plate to drive the exothermic reaction. The heat generated from the oxidation catalyst is efficiently transferred between the two catalysts through the thin metal plate. The prototype was tested and demonstrated rapid startup, fast transient response, 20:1 turndown ratio, and stable temperature control.

Approach

The development of plate reactor designs for conversion of gasoline to hydrogen requires the integration of the reactor design with details of the catalyst's performance. To integrate all of these aspects and optimize the design, this project makes

extensive use of reactor modeling that includes all important aspects of the system, e.g., convective gas flow, diffusion, catalyst layer structure, heat transfer throughout the structure and detailed kinetics of the catalytic reactions. Because reaction kinetics are not readily available in many cases, initial work was directed at developing catalyst materials with activity in the desired operating range that could be applied as a washcoat layer onto the plate surface. The kinetics of the catalytic reaction was then measured in sufficient detail to allow modeling of the plate reactor design using in-house developed computer codes for each reactor design.

The resulting target reactor design and catalyst system were then used to develop mechanical designs for a plate reactor to be used in laboratory demonstration at the 3-kW(e) size. Test results were fed back into the model to refine assumptions and validate the model. Design improvements are evaluated within the model before designing and procuring hardware.

Results

Prototype Testing

Using CESI's background and expertise in catalyst development, catalyst coating methods, mechanical stress analysis, and experimental design, a prototype SR plate reactor was designed, built, and tested. The fuel used for all of the tests was Argonne National Laboratory (ANL) Benchmark Fuel I doped with 10 ppm sulfur. Because startup time is one of the more critical targets to meet for on-board fuel processing, initial tests were performed in order to determine the shortest possible startup time. Figure 1 illustrates that a plate reactor can achieve its full operating temperature within 70 seconds. There is opportunity to improve this startup time by reducing heat loss, improving flow distribution, and reducing the plate material thickness. By incorporating these improvements, startup times less than 60 seconds can be easily achieved.

Prototype testing also demonstrated a load turndown ratio of 20:1 that meets the DOE's 2004 turndown target. Figure 2 illustrates that the turndown is achieved while maintaining relatively constant reactor temperatures.
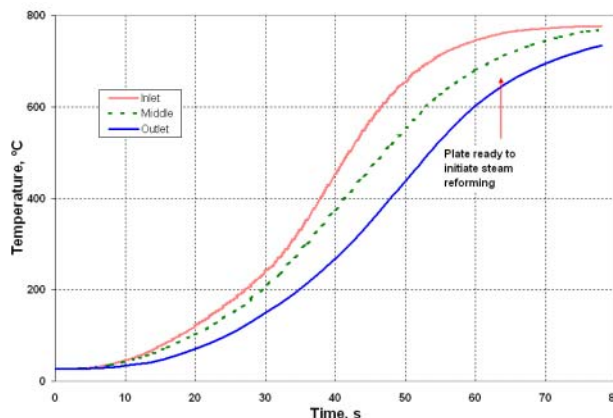

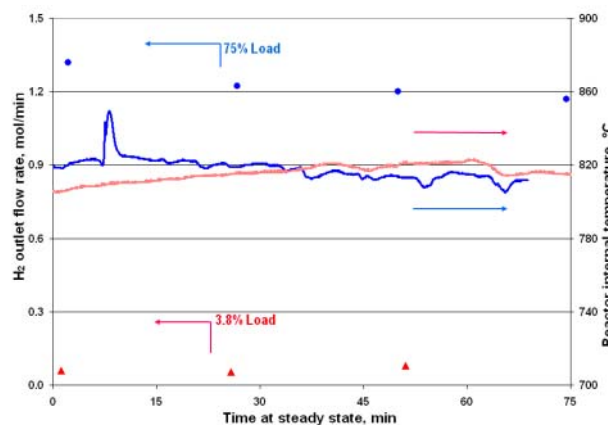**Figure 1.** Temperatures at Different Locations along the Length of the SR Plate Reactor During Startup

Figure 2. 20:1 Turndown Performance of the SR Plate Reactor While Maintaining Target Operating Temperature

Figure 3 plots the H_2 output and reactor temperature for several load changes. This data illustrates the prototype plate reactor's ability to handle a 20% load per second transient. Improvements to the control system will allow larger step changes in load within the same time period to demonstrate the reactor's transient performance capabilities.

Modeling

Detailed modeling has been developed in order to minimize the startup time for an integrated 50-kW(e) fuel processing system. After evaluating several different models, it was determined that the simultaneous heating of the SR, WGS and PrOx
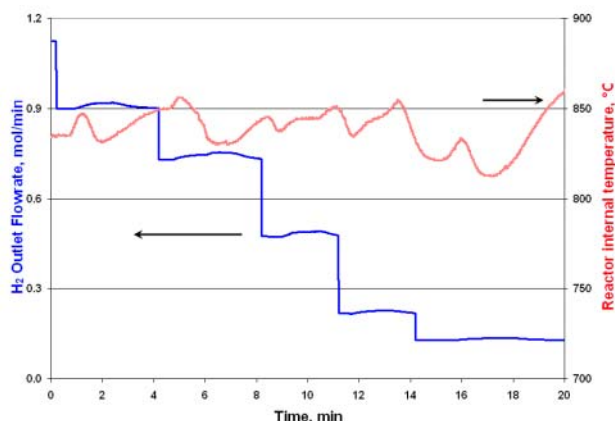
Figure 3. Changes in H_2 Outlet Flowrate and Reactor Internal Temperature During Transient Step Changes In Load

reactors using high-temperature air flow rates could enable all three reactors to reach their corresponding light-off temperatures within 10 seconds. This, however, would require an instantaneous supply of hot air, such as from a combustor.

The efficiency of an integrated fuel processor was calculated using Pro/II SimSci. Various operating parameters were modified to quantify their impact on overall system efficiency. The baseline system efficiency was calculated to be 79.5%. Several performance improvements were identified that could achieve a system efficiency of 83.6%.

Catalysts Development

Steam Reforming. SR catalyst efforts were directed at improving performance in terms of activity, durability, and operating range while reducing catalyst cost. Even though the SR catalyst is not yet optimal, a CESI-developed catalyst was selected to determine the kinetic parameters of the SR reaction, which was essential to the modeling of the SR plate reactor. All the SR kinetics experiments have been conducted using ANL Benchmark Fuel I doped with 10 ppm sulfur.

Even though the gas chromatography analysis shows that a variety of intermediate C2 to C8 hydrocarbons are formed during the reforming reaction, the kinetic model was limited to the formation of C1s (CO, CO_2, and CH_4) since these components account for a majority of the

endothermicity of the reaction. The resulting kinetic expression takes the form of the following 3-parameter power-law type of equation:

$$r = \frac{dN_{C1}}{Wdt} = k_0 \cdot \exp\left(\frac{-E_A}{RT}\right) \cdot y^a_{HC}$$

The experimental data and fit of the data using the above expression is shown on Figure 4. This type of steady-state expression is valid only in a relative narrow range of operating conditions, namely 3.5 < Steam/Carbon (S/C) < 4 and T > 775°C. This expression and these rate constants were successfully incorporated into the SR plate reactor model.

Water Gas Shift. A systematic approach to verify the reproducibility of the WGS catalyst performance results has been performed in the wall-coated tubular reactor. By testing several different samples of the same catalyst formulation, CESI was able to demonstrate that the wall-coated reactor design is appropriate to assess the performance of a catalyst. The variability of the results obtained within the tests, illustrated in Figure 5, was minimal.

With this experiment, CESI demonstrated that the wall-coated tubular reactor is appropriate to demonstrate consistent catalyst performance results. The improved control of the catalyst temperature and mass loading in the wall-coated tubular reactor is the likely explanation for the high level of reproducibility in comparison to earlier experiments in the fixed bed reactor. Durability runs of 500 hours extrapolated to 2000 hours, using traditional
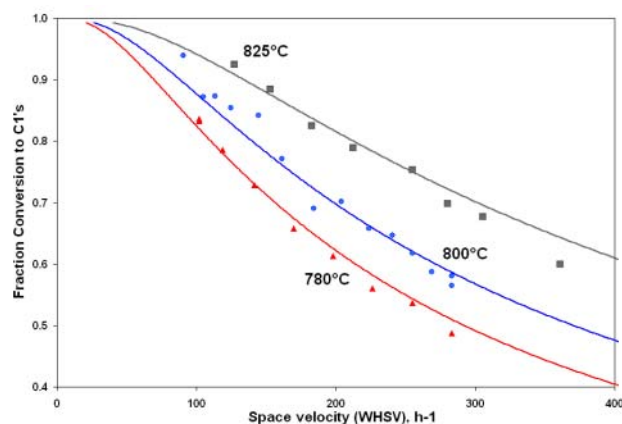

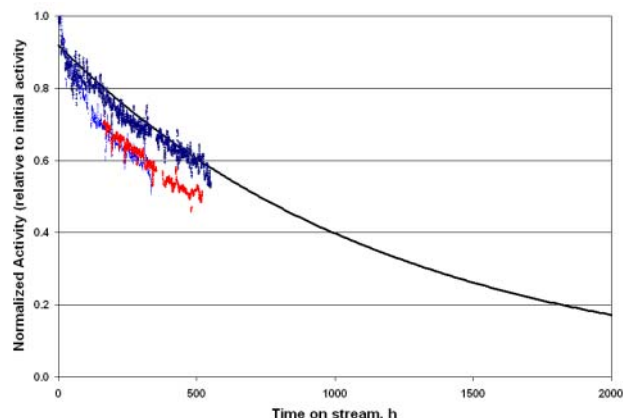**Figure 4.** SR Kinetic Data and Rate Expression Fit of the Data

Figure 5. Results of Multiple WGS Experiments Illustrating the Minimal Variability Between Tests

Figure 6. CO Outlet Concentration versus Temperature for a CESI-Developed PrOx Catalyst Operated in Single-Stage Mode at a Constant Space Velocity

exponential deactivation rate, demonstrated that a significant improvement in the initial activity or in durability is required to achieve the target of 5 kg of WGS catalyst for a 50-kW(e) fuel processor.

Preferential Oxidation. CESI's leading PrOx catalyst formulation is able to reduce a 1.0% CO concentration feed to below 10 ppm CO in the presence of water in the stream and shows no deactivation after 800 hours of continuous operation. Typical PrOx performance is shown in Figure 6. One approach to reducing the size of the WGS reactor in the fuel processor is to reduce the duty on the WGS reactor and increase the inlet CO concentration to the PrOx reactor. In this approach, the overall efficiency of the fuel processor system is slightly penalized, but the gain in terms of WGS reactor volume is substantial (due to both the WGS reaction being carried out at a higher temperature and the WGS duty being lower). CESI demonstrated that its leading PrOx catalyst's performance could be adjusted to such a fuel processor system configuration. The PrOx catalyst was tested with an inlet CO concentration of 1.8% and achieved, in a single-stage reactor, a reduction of CO to 10 ppm.

Conclusions

- The results from the prototype testing demonstrate that the plate reactor concept is a viable SR reactor design. The demonstrated startup time, turndown capability, and transient
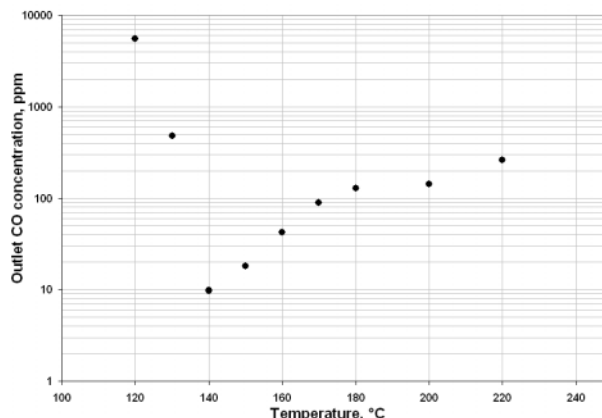
performance support the use of a SR plate reactor for on-board fuel processing.
- Experimentally measured SR and combustion kinetics have been successfully integrated in a model of the plate reactor.
- PrOx catalyst has been proven stable, resistant to steam, and able to perform a high CO conversion in a single-stage reactor.

FY 2004 Publications/Presentations

1. "System Integration of a Plate Reactor for Gasoline Steam Reforming for Automotive Applications", 2003 Grove Fuel Cell Symposium, 24-26 September 2003, London, UK.

2. "System Integration of a Plate Reactor for Gasoline Steam Reforming for Automotive Applications", 2003 Fuel Cell Seminar, 3-7 November 2003, Miami Beach, FL.

3. "Plate Based Fuel Processing System", FreedomCAR Technical Team Review, 18 February 2004, Washington, DC.

4. "Plate Based Fuel Processing System", Hydrogen, Fuel Cells and InfrastructureTechnologies Program, 2004 Annual Program Review, 24-27 May 2004, Philadelphia, PA.